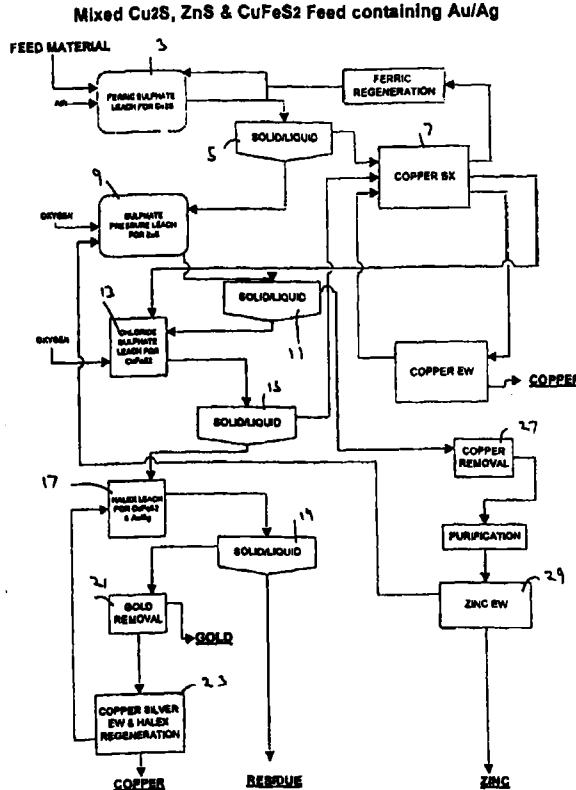




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C22B 3/06, 3/08, 3/10, 3/22, 3/26, 3/42, 15/00, 19/02, 19/20, 11/00, 11/06		A1	(11) International Publication Number: WO 00/11228 (43) International Publication Date: 2 March 2000 (02.03.00)
<p>(21) International Application Number: PCT/AU99/00679</p> <p>(22) International Filing Date: 24 August 1999 (24.08.99)</p> <p>(30) Priority Data: PP 5437 24 August 1998 (24.08.98) AU</p> <p>(71) Applicant (<i>for all designated States except US</i>): TECHNOLOGICAL RESOURCES PTY. LTD. [AU/AU]; 55 Collins Street, Melbourne, VIC 3000 (AU).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (<i>for US only</i>): SHAW, Raymond, Walter [AU/AU]; 29 Kirribilli Road, New Gisborne, VIC 3438 (AU).</p> <p>(74) Agent: GRIFFITH HACK; 509 St Kilda Road, Melbourne, VIC 3004 (AU).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: HYDROMETALLURGICAL EXTRACTION OF COPPER AND OTHER VALUABLE METALS</p> <p>(57) Abstract</p> <p>A hydrometallurgical process for extracting copper and any one or more than one of zinc, silver and gold from a sulphide ore or concentrate is disclosed. The process includes a range of mineral species that contain copper and one or more than one of zinc, silver and gold, which process includes two or more than two leach steps using each liquors of different composition, each leach step selectively leaching one or more than one metal from the minerals. The process also includes separating a solid residue and an exit leach liquor after each leach step, leaching the solid residue produced in each leach step in a successive leach step, and recovering metal from the exit leach liquor produced in each leach step.</p>			



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

HYDROMETALLURGICAL EXTRACTION OF COPPER AND OTHER VALUABLE
METALS

5

The present invention relates to hydrometallurgical extraction of copper and other valuable metals from sulphide ores and concentrates.

10

The present invention relates particularly, although by no means exclusively, to hydrometallurgical extraction of copper and one or more than one of the metals zinc, gold and silver from sulphide ores and concentrates.

15

There are limited known hydrometallurgical options for treating copper sulphide ores and concentrates to extract copper.

20

The bulk of copper produced hydrometallurgically on a commercial basis is from solvent extraction and electrowinning plants based on acid heap leaching of ore or from bacterially assisted dump leaching of low grade sulphuric wastes.

25

However, heap leaching is not a commercial option for a number of ores, particularly those containing refractory sulphide minerals such as chalcopyrite. Heap leaching of chalcopyrite ($CuFeS_2$) ores results in poor recoveries and low extraction rates which in turn lead to the need for large leach areas and low copper content in the pregnant liquor for the solvent extraction and electrowinning steps. The non-recovery of gold is also a deterrent in cases where there is the option to produce a concentrate. Residual copper largely prevents further processing to recover gold in the heap.

Heap leaching is also not practised for zinc

recovery from sulphide ores because of the difficulty in obtaining a liquor suitable for subsequent economic recovery of the zinc.

5 The three hydrometallurgical processes with most potential for chalcopyrite-rich sulphides are currently the Intec process, the BHAS process, and the related Cominco (CESL) process. Successful laboratory and/or pilot testing of these three processes has been reported. The processes
10 all rely on the presence of chloride to improve the leaching efficiency for chalcopyrite without excessive attack on pyrite and oxidation of sulphur to sulphate. The BHAS/Cominco processes use conventional solvent extraction/electrowinning technology to recover copper,
15 whereas the Intec process uses a particular novel chloride electrowinning step which produces copper powder. The BHAS process has been operated successfully on a chalcocite (Cu₂S) like feed for more than ten years. However, the Intec, BHAS, and Cominco processes have not been operated
20 commercially for chalcopyrite ores or concentrates.

There has also been considerable development of processes based on using high pressure and temperature (>200C) oxidative acid sulphate leaching of copper
25 concentrates. These have not been commercially successful presumably because of the high costs associated with the conversion of the sulphur present to sulphate and the difficulties with economic recovery of gold and silver present from the residue using conventional cyanide based
30 technology.

There is also active development of sulphate-based solvent extraction/electrowinning processes based on ferric sulphate leaching, low temperature
35 oxidative pressure leaching, and bio-leaching. These processes are largely targeting the more readily leached sulphide minerals, such as chalcocite, rather than the more

difficult to leach ores, such as chalcopyrite. There are no known commercial copper operations using any of these technologies.

5 An object of the present invention is to provide an alternative process for economic treatment of copper containing sulphide ores and/or concentrates which also contain associated valuable metals such as zinc, gold or silver.

10 According to the present invention there is provided a hydrometallurgical process for extracting copper and any one or more than one of zinc, silver and gold from a sulphide ore or concentrate which includes a range of 15 mineral species that contain copper and one or more than one of zinc, silver and gold, which process includes two or more than two leach steps using leach liquors of different composition, each leach step selectively leaching one or more than one metal from the minerals, separating a solid 20 residue and an exit leach liquor after each leach step, leaching the solid residue produced in each leach step in a successive leach step, and recovering metal from the exit leach liquor produced in each leach step.

25 It is preferred that the process of the present invention includes 2 or more of the leach steps summarised below which are tailored to selectively attack minerals so that each metal is recovered through a leach step (or steps) that is suitable to the minerals and the leach steps 30 are complementary in terms of allowing materials transfer between them without one step being detrimental to and seriously interfering with the next step. The leach steps are set out below in order of increasing aggressiveness.

35 1. A ferric sulphate leach step to extract copper from chalcocite (Cu₂S) in the sulphide ore or concentrate. This leach enables use of simple

- 4 -

atmospheric reactors, gives good copper extraction, and allows regeneration of the leachate using bacteria or pressure oxidation of the liquor. This leach step will also dissolve part of any zinc that is present and some of the slightly more refractory copper minerals but is not ideally suited to high zinc feed. This leach does not dissolve gold or silver which remain in the residue.

10

2. A pressure oxidation leach in acid sulphate media with oxygen injection to extract zinc from sphalerite (ZnS). In the sulphide ore or concentrate as a first leach step or a leach step on the solids product of the ferric sulphate leach step. This leach step was originally developed by Sherritt-Gordon. This leach can also potentially dissolve copper from primary sulphides but is not very efficient for more refractory minerals such as chalcopyrite. Copper which leaches may be removed from the liquor with solvent extraction or alternatively may be precipitated into the residue by maintaining a moderately high pH (around 4) and then re-leached using one or other of the alternative leach steps. This leach does not dissolve silver or gold.

15

20

25

3. A mixed chloride-sulphate leach to extract copper from copper rich concentrates containing valuable levels of refractory sulphide minerals such as chalcopyrite in the sulphide ore or concentrate as a first leach step or as a leach step on the solids product of the ferric sulphate or the pressure oxidation leach steps and not amenable to leaching in sulphate-only systems. This leach step will dissolve virtually all copper sulphide

30

35

- 5 -

minerals and zinc from sphalerite. Silver and gold remain in the residue.

4. A halex leach as described in the Intec process
5 to extract copper, silver and gold from solids
products materials. This leach step is described
as part of the Intec process where it is used to
leach chalcopyrite and produce copper powder
through a chloride electrowinning step. This
10 leach will dissolve all zinc and copper minerals
as well as the silver and gold.

5. An oxidative acid sulphate high pressure, high
15 temperature leach carried out at over 200C such
that much of the sulphur present is converted to
sulphate and copper and zinc present are leached
into the liquor. This leach step has been
described in numerous publications such as those
20 of Dreisinger, or as part of a Sherritt-Cominco
process. Although this leach is more aggressive
to the sulphur and copper than even the halex
leach it does not dissolve the gold or silver. In
the invention proposed it is potentially used as
25 an alternative to leach step 3 in special
circumstances where there is a wish to
deliberately convert significant amounts of the
sulphur to sulphate.

The capability of the more aggressive leach steps
30 summarised in items 3,4 and 5 above to dissolve more of the
valuable metals does not of itself mean that it is
preferable to use them as a substitute for the multi-staged
approach of the present invention. These more aggressive
leach steps have penalties associated with the complexity
35 of the leach and the cost of subsequent metal recovery.
Leach steps 3 and 4 both include chlorides which prevent
simple direct electrowinning of zinc and requires use of

- 6 -

solvent extraction which is not to date very efficient for zinc. Similarly the need for tonnage oxygen and the greater complexity of using pressure vessels and/or chloride resistant construction detracts from the use of 5 these more aggressive leach steps if the copper-containing minerals present are readily leachable in a simple ferric sulphate liquor.

10 The present invention is described further by way of example with reference to Figures 1 to 5 which are flow sheets of preferred embodiments of the process of the present invention.

15 The process illustrated in Figure 1 combines the 4 leach steps summarised in items 1 to 4 above and is applicable to sulphide ores and concentrates that include chalcocite (Cu_2S), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), gold and silver.

20 The feed material is initially leached in ferric sulphate leach 3 to dissolve the readily-leached copper. The time, temperature and oxidation potential of this leach are controlled such that copper is selectively extracted over zinc. Some zinc dissolution may occur leading to a 25 build up in the circuit but this can be balanced by the soluble zinc contained in the entrained liquor fed to the subsequent leach stages with the solid residue.

30 The solids are separated from the liquor in a solid/liquid separation step 5 and the liquor is then transferred into an electrolyte for copper electrowinning in a solvent extraction step 7.

35 Ferric ions are partially converted to ferrous during the ferric sulphate leach 3 and the majority of the ferrous ions are regenerated to ferric ions and returned to the ferric sulphate leach 3 using bacteria or pressure

- 7 -

oxidation. The leach and the regeneration can be carried out simultaneously in one pressure vessel but this has penalties in complexity of equipment and also in possible lack of selectivity of the leach.

5

The solid residue from the solid/liquid separation step 5 is leached in a sulphate pressure leach 9 in an acid sulphate liquor with injection of oxygen at elevated pressure and temperature (around 150psi, 150C) to 10 dissolve the zinc present and to give a solution suitable for purification and zinc electrowinning.

The transfer of residual sulphate and iron from the ferric sulphate leach 3 into this leach does not cause 15 difficulties as the sulphate pressure leach is also sulphate based and is capable of precipitating the iron as jarosite and/or goethite. This leach would be as currently practiced in existing commercial plants unless there is excessive copper present in the liquor due to inadequate 20 washing from the ferric sulphate first leach 3, or because the feed material has minerals present such as bornite which are midway in reactivity between chalcocite and chalcopyrite. Alternative approaches are to force the copper in liquor to precipitate by pushing the pH up to 25 where the cupric ions present become much less soluble or to add a specific copper extraction step such as solvent extraction into the circuit to economically recover the copper. The final traces of copper could then be removed using the conventional cementation reaction in the zinc 30 dust purification step.

The presence of elevated levels of copper in the zinc liquor as would occur if this leach step was used directly on a copper zinc ore can lead to some difficulties 35 in subsequent processing. Removing this copper by solvent extraction generates acid in the zinc liquor which requires neutralisation prior to final purification and

- 8 -

electrowinning. Although this neutralisation can be done with lime which generates gypsum there is a significant cost penalty associated. The approach of a combined leach of the copper and zinc is therefore generally not favoured
5 for a stand alone operation. At specific locations there may be scope to overcome this problem through having available zinc oxide such as from a conventional roast-leach circuit, or a copper free zinc sulphide concentrate, for this "neutralisation". In that situation there is scope
10 to consider using this pressure leach step to extract both the readily leachable copper and the zinc.

Part of the zinc in the feed material may leach during the ferric sulphate leach 3 but this does not
15 transfer across the copper solvent extraction step 7 and goes to the sulphate pressure leach step 9 in the liquor which accompanies the solid residue from the solid/liquid separation step 5.

20 In cases where the zinc is extremely reactive there may be a need to neutralise some liquor to force more zinc out and prevent it building to an unacceptably high level. An alternative is to remove the zinc from part or all of the raffinate liquor from copper solvent extraction
25 using zinc solvent extraction and to transfer it into a conventional high zinc acid sulphate solution for electrowinning. This may require prior removal of any residual cupric ions present in the liquor being fed to zinc solvent extraction using cementation and/or ion exchange.
30

The product of the sulphate pressure leach 9 is transferred to a solid/liquid separation step 11.

35 The liquor from the solid/liquid separation step 11 is transferred successively to copper removal 27, purification, and zinc electrowin 29.

The solid residue from the solid/liquid separation step 11 contains undissolved copper present in refractory minerals such as chalcopyrite plus the precious metals silver and gold. It also contains any oxide waste materials from the original feed material, unreacted waste sulphides such as pyrite, elemental sulphur, and precipitated iron in the form of jarosite and/or goethite arising during the leach reactions.

10

The solid residue from the solid/liquid separation step 11 is leached in a mixed acid chloride-sulphate leach 13 to extract the copper without redissolving the iron compounds or significantly attacking any pyrite present. The chloride-sulphate leach 13 avoids converting much of the elemental sulphur to sulphate. Once again forward transfer of sulphate containing liquor is not of major concern because of the sulphate base of the mixed chloride sulphate step. Any untoward build up of sulphate can be accommodated by deliberate precipitation preferably as a jarosite or through limited amounts of gypsum using lime/limestone additions.

The product of the chloride-sulphide leach 13 is transferred to a solid/leach separation step 15.

The copper-bearing liquor from the solid/liquid separation 15 is subjected to solvent extraction 7 to transfer the copper to a sulphate liquor for conventional electrowinning. If the liquor contains significant zinc due to inefficiencies in the sulphate pressure leach 9 there may be advantages including a zinc solvent extraction step to also transfer the zinc into a sulphate liquor for electrolysis. This may require first removing all of the cupric ions from the liquor probably through solvent extraction followed by ion exchange and/or cementation with zinc. An alternative where chloride is present in the

- 10 -

liquor is to reduce the cupric ions to cuprous and rely on the chloride ions present to allow this to be stable in the liquor. The leach would oxidise these cuprous ions to cupric and allow recovery when the liquor is recycled for use.

5 In unusual circumstances where the ore or concentrate contains significant levels of acid consuming minerals, and/or there is a site specific need to produce 10 some sulphuric acid at a greater rate than the small amount which arises in the chloride sulphate leach, there may be 15 advantages in substituting a high pressure, high temperature leach (as discussed as leach type 5) for the chloride-sulphate leach 13. The remainder of the flowsheet 15 would remain unaltered with the copper leached still being recovered via solvent extraction and the residue proceeding to the next step 15.

20 The solid residue from the solid/liquid separation step 15 contains gold and silver and a small amount of undissolved copper. This residue is leached in a halex leach 17 to extract gold, silver and residual copper into solution. Small amounts of residual liquor transferred from the preceding leaches is readily managed by 25 precipitation of the contained sulphates as gypsum using lime/limestone. Residual chloride is compatible with the halex leach solution and is not of concern.

30 The liquor and the residual solids are separated in a liquid/solid separation step 19 and the solids are washed and neutralised for disposal. The liquor from the solid/liquid separation step 19 is then passed through carbon columns 21 to extract gold.

35 There may be a need to partially treat the liquor with metallic copper or another reductant prior to entry to the carbon columns 21 to ensure the redox potential is of

- 11 -

the right order for the gold to transfer onto the carbon.

The gold depleted liquor from the carbon columns 21 is then fed into an electrowinning cell 23 to recover 5 the copper and silver and regenerate the halex. The cell is designed so that the halex and cupric ions generated at the anode are largely prevented from returning to the cathode. This can be achieved as is done in many industries through the use of ion selective membranes as 10 physical barriers. An alternative approach is to design of the cell geometry in terms of inlet and outlet arrangement, the use of stirrers and baffles and the possible inclusion of porous membranes such that the electrolyte predominantly flows from the vicinity of the cathode to that of the anode 15 without backflow or back mixing.

There are a number of alternatives for this part of the process depending upon the relative amounts of the copper and silver, and also on other impurity elements that 20 may be present. The preferred approach is to electrowin the copper and silver directly from the liquor without prior purification. This would give an impure product and also consume more power than is the case where halex leaching is being used as the primary copper production but 25 avoids additional processing steps. The copper product in this arrangement would need further treatment to give normal high purity copper and recover the silver. This can be done using conventional copper electrorefining by melting the powder and casting it into anodes. In special 30 cases there may be advantages in removing the silver from the liquor prior to electrowinning and purifying the liquor as proposed in the published Intec process to give a higher purity copper powder product for direct sale. This may also be beneficial if there are significant levels of mercury 35 present in the feed to ensure it reports to a solid residue rather than into the copper metal.

In some situations, there may be advantages in reacting this liquor with a small amount of reactive copper material such as scrap metal, but if these were unavailable even a reactive primary sulphide such as chalcocite, to 5 take advantage of the residual oxidative power and convert the majority of the cupric ions present to cuprous prior to electrowinning.

The flowsheet of Figure 1 covers the case where 10 the feed material contains both of the most common copper minerals plus economically significant levels of zinc, silver and gold. This is not always the case and the process can readily be modified based around the criteria of including the leach steps most suitable for the specific 15 minerals present.

The flowsheets of Figures 2 to 5 are examples of modified processes, as summarised below.

20 Figure 2: Cu₃S - Au/Ag feed material.

The process includes the ferric sulphate 25 leach for the majority of the copper followed by the halex leach for the residual copper and the silver and gold.

Figure 3: CuFeS₂ - Au/Ag feed.

The process includes the chloride-sulphate 30 leach for the majority of the copper followed by the halex leach for the residual copper and silver and gold.

35 Figure 4: ZnS - CuFeS₂ feed without Au/Ag.

The process includes sulphate pressure leach for the zinc followed by a chloride-sulphate

leach for the copper.

Figure 5 Cu₂S - ZnS feed.

5 The process includes the ferric sulphate leach followed by the zinc pressure leach.

The underlying technical and economic logic for the above described process methodology is as follows:

10 1. The ferric sulphate leach system can efficiently extract copper from chalcocite (Cu₂S) and solvent extraction can readily transfer copper from low concentration leach liquor into an electrolyte for electrowinning. The solvent extraction reagents are selective for copper and thus also provide the purification step. Pressure leaching in air and/or oxygen can also leach copper from chalcocite but is more expensive in terms of equipment needed and are less selective for copper over other minerals such as sphalerite and pyrite. The use of pressure is more favoured as a means of regenerating ferric ions from ferrous ions formed during the leach stage as an alternative to bacterial regeneration in cases where suitable bacteria are unavailable and/or the impurities in the feed are toxic to bacteria and render this method unsuitable.

20 25 30 35 The zinc pressure leach can also be used to dissolve copper from these primary sulphide minerals but this can limit the options for the zinc step in terms of needing to balance acidity in the system, and in being able to recover the copper. For feed with significant chalcocite content the separate step is preferred. For feed where chalcocite is not a major copper mineral,

- 14 -

the use of a separate ferric sulphate leach may not be warranted with the subsequent leach steps being used to also recover the copper present in this form.

5

3. Solvent extraction of zinc is not currently attractive given the lack of a cheap selective reagent which is not sensitive to other metals. The ZENECA reagent is currently the most 10 promising but is expensive relative to other reagents and may remain so, cannot tolerate the presence of cupric ions, and needs extra treatment to handle cadmium. These issues coupled with, by comparison to copper, a higher 15 power usage in zinc electrowinning and lower sale price suggest that if the zinc content of a feed is significant then the majority of it should be recovered directly to a sulphate electrolyte. This drives the process towards the sulphate 20 pressure leach for zinc with solvent extraction systems only being used to recover metal from side streams.

25

30

35

4. The use of a chloride-sulphate leach to extract copper from minerals such as chalcopyrite is favoured. This is more expensive than the simple ferric sulphate leach as it requires tonnage oxygen and chloride resistant equipment but does give good dissolution of the minerals which the ferric sulphate leach will not readily attack. It can be carried out under atmospheric conditions but may also be done under elevated pressures to enable higher temperatures (120C) and faster reaction rates. This leach step can selectively dissolve copper without conversion of the sulphur to sulphate and attack on the pyrite as occurs using high temperature (>200C) sulphate

- 15 -

pressure leaching. This higher pressure and temperature leaching can be used as an alternative if there is a special need to convert much of the sulphur present to sulphate to provide a source of sulphuric acid. This is a much more expensive leach process and is generally not favoured. Copper in the chloride-sulphate liquor can readily be transferred into a sulphate electrolyte using the same process as for the ferric sulphate leach. This avoids the need for electrowinning from chloride containing liquor as is the case in processes such as the Intec and CLEAR processes. Electrowinning from chloride liquor is complex in terms of needing diaphragm cells, and gives a powder product rather than the conventional cathode sheet obtained from sulphate.

5. The use of a halex leach to recover gold and silver from residues from any one or all of the other leaches overcomes the issue of excessive reagent consumption found when conventional cyanide leaching is used. Residual copper and the presence of elemental sulphur both interfere with normal cyanidisation and have been a barrier to treatment of residues of this type. The halex provides a sufficiently high redox potential to extract gold and maintain it in solution for transfer onto carbon and subsequent recovery. This leach also dissolves silver and any residual copper not extracted in previous leach steps.

6. Using the halex leach only for the residue to recover the precious metals and small amounts of copper avoids concerns on the quality of the copper powder produced and on the efficiency of the electrowinning step by comparison with the

- 16 -

conventional sulphate electrowinning. This application of the halex leach- electrowinning step therefore differs from that proposed in the Intec process where it is being used to extract 5 copper directly from chalcopyrite concentrates as the only production route. Using this step primarily for the recovery of gold and silver from the residue from an acid sulphate based leach, the tonnage of metal being produced via 10 this technology is sufficiently small that the use of a chloride-bromide electrowinning step to recover the copper and silver, and to regenerate the halex is acceptable. Attaining a high electrowinning efficiency in this step is not 15 critical to the overall economics as it is only one small part of a much larger situation within the overall economics. In this format the eventual copper product is predominantly conventional electrowon cathode rather than 20 tonnage quantities of powder with the powder being refined to produce conventional refinery cathode.

25 The following is a more detailed description, by way of example, of the process shown in Figure 4.

In general terms, the process shown in Figure 4 includes:

30 (a) subjecting a concentrate of a copper sulphide ore which contains, chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) to a sulphate pressure leach to extract into solution a substantial proportion of the zinc, and 35 thereafter;

(b) subjecting the solid residue and liquid

- 17 -

products of the sulphate pressure leach to largely separate (but to a certain extent interrelated) circuits to extract copper and zinc from the products.

5

With reference to Figure 4, the concentrate is supplied to a single stage sulphate pressure leach 33 which extracts into solution greater than 90%, preferably greater than 95%, of the zinc, moderate amounts of copper 10 (preferably <20%), and relatively low amounts of iron after two hours leaching at 150°C.

The iron reports as goethite or jarosite depending on conditions.

15

In general terms, the amount of zinc in the solid residue of the concentrate that remains after sulphate pressure leach 33 should be minimised because zinc increases the cost of the subsequent process steps to 20 remove copper from the residue.

The sulphate pressure leach 33 should run with little/no excess acid to achieve a low iron liquor. In addition, the residue may require an acid repulp in the 25 zinc spent electrolyte prior to final separation.

The sulphate pressure leach 33 may also be influenced by the level of formation of plumbago-jarosite and the impact of this on sulphate balance and subsequent 30 treatment. Limestone is an alternative means of removing sulphate, although the residue would probably need to be filtered and washed before passing to the copper circuit to minimise zinc and acid transfer.

35

The product of sulphate pressure leach 33 is transferred to a solid/liquid separation step 35 which separates the product into a solid residue and a zinc-rich

liquor.

5 The zinc-rich liquor from the solid liquid separation step 35 is transferred to the zinc extraction circuit.

10 The first step in this circuit is solvent extraction 39 to separate copper from the liquor. Conventional copper solvent extraction reagents can be used to selectively extract the copper from this relatively low acid liquor, and the only issue is the need for reasonable washing to reduce the level of physical zinc carryover into the electrolyte.

15 The copper-rich liquor from solvent extraction 39 is transferred by line 40 to the copper extraction circuit. This is an optional step and there may be advantages in considering the version of the Cominco process where the pressure sulphate leach is sufficiently acid starved so 20 that copper sulphate is precipitated. This copper sulphate would readily redissolve in the subsequent copper leach in the copper extraction circuit described in more detail below. This may be advantageous if too much of the copper leaches during the sulphate pressure leach as it would 25 reduce the amount of copper to be removed by solvent extraction in the zinc extraction circuit.

30 The exact arrangement of whichever option is chosen will depend upon leach behaviour and on the preferred means of separating the residue. The BHAS process uses a simple two stage leach with the second step being at high solids and high acid to enhance recovery in a short residence time. The decision on whether or not to attempt to recover lead and precious metals strongly 35 influences whether to make a single residue or whether there are advantages in producing a separate iron residue. Arranging the leach circuit to minimise plumbo-jarosite

- 19 -

formation may be important if residue treatment is included. The flow sheet gives the simplest version as a base case.

5 The equipment size and hence costs is largely set by the volumetric flow and there are advantages in running high zinc and copper pickup in the process. The main limitation on this is the transfer capability of the solvent extraction steps.

10 The zinc-rich, copper-depleted liquor from solvent extraction 39 is subjected to conventional zinc dust purification 41 and electrowinning 42 to recover zinc. Depending upon the amount of copper removed in the solvent 15 extraction step 39, and the acid generated, a small amount of neutralisation may also be needed to avoid excessive zinc dust usage. This would preferably be done using zinc scrap or zinc oxide unless they were unavailable and/or there was a need to also remove some excess sulphate in 20 which case limestone and/or lime would be preferred.

The solid residue from sulphate pressure leach 33 is transferred to the copper extraction circuit.

25 The first step in this circuit is a chloride sulphate leach 37 which dissolves copper from the chalcopyrite the solid residue without significant attack on pyrite and without significant sulphate formation. The leach is carried out with continuous oxygen injection at 30 around 90-110°C. The options for the leach are an atmospheric or low pressure version using higher chloride (15-60g/l) based on the BHAS process or with greater pressure assistance at lower chloride levels (10-15g/l) as piloted and patented by Cominco. Both of these options 35 have been shown to give high copper extractions in laboratory tests.

- 20 -

After solid/liquid separation 38, the copper-rich, zinc-depleted pregnant liquor is fed to solvent extraction 15 to selectively transfer copper to a chloride free electrolyte.

5

The copper-rich liquor from solvent extraction 45 is transferred to electrowinning 50 to recover copper.

10 The copper-depleted liquor from solvent extraction 45 is split into a return stream that is transferred from by line 47 to the chloride sulphate leach 37 and a stream that is transferred by line 49 for treatment to remove zinc and to maintain sulphate and impurities balance. The bleed stream is passed through 15 copper removal 50 and then solvent extraction 51 to separate zinc from the liquor. Any suitable means, such as solvent extraction, sulphidisation or cementation, may be used to remove copper. The low copper/zinc liquor stream is neutralised and discharged or recycled depending on 20 overall water balance.

25 The proportions of each stream depend on the efficiency of zinc extraction in sulphate pressure leach 33, and in the level of washing of the residue. Zinc solvent extraction 32 is not commonly practised commercially because of the high cost and poor pickup and selectivity of the available reagents.

30 Both copper electrowinning 50 and zinc electrowinning 42 are based on commonly practised conventional technology. The electrolytes generated through the copper and zinc circuits are selected to give high grade products. The process does not include specific halide or manganese removal steps but these may need 35 consideration dependant upon the ore composition and water quality.

- 21 -

The solid residue from solid/liquid separation 43 is either neutralised and dumped or treated to recover any unleached Cu/Zn sulphides for recycle, and to produce a lead bullion containing the precious metals for sale. An 5 alternative approach is to use flotation to remove the sulphur and sulphides, possibly selectively, followed by arc furnace matte/bullion smelting.

Many modifications may be made to the process of 10 the present invention described above without departing from the spirit and scope of the invention.

CLAIMS:

1. A hydrometallurgical process for extracting copper and any one or more than one of zinc, silver and gold from a sulphide ore or concentrate which includes a range of mineral species that contain copper and one or more than one of zinc, silver and gold, which process includes two or more than two leach steps using leach liquors of different composition, each leach step selectively leaching one or more than one metal from the minerals, separating a solid residue and an exit leach liquor after each leach step, leaching the solid residue produced in each leach step in a successive leach step, and recovering metal from the exit leach liquor produced in each leach step.

2. The process defined in claim 1 includes 2 or more of the leach steps which are tailored to selectively attack minerals so that each metal is recovered through a leach step (or steps) that is suitable to the minerals and the leach steps are complementary in terms of allowing materials transfer between them without one step being detrimental to and seriously interfering with the next step.

3. The process defined in claim 1 or claim 2 includes a ferric sulphate leach which extracts copper from chalcocite (Cu_2S) in the sulphide ore or concentrate or the solids residue of a previous leach step.

4. The process defined in claim 3 includes selecting the time, temperature and oxygen potential of the ferric sulphate leach to leach copper over zinc.

5. The process defined in claim 3 or claim 4 includes carrying out a solids/liquid separation step after the ferric sulphate leach and forming a solid residue and

an exit leach liquor.

6. The process defined in claim 5 includes recovering copper from the exit leach liquor.

5

7. The process defined in any one of the preceding claims includes a pressure oxidation leach in acid sulphate media with oxygen injection which extracts zinc from sphalerite (ZnS) in the sulphide ore or 10 concentrate or the solid residue of a previous leach step.

8. The process defined in claim 7 includes carrying out the pressure oxidation leach at a temperature in the range of 140 to 160°C.

15

9. The process defined in claim 7 or claim 8 includes carrying out a solids/liquid separation step after the pressure oxidation leach and forming a solid residue and an exit leach liquor.

20

10. The process defined in claim 9 includes recovering zinc from the exit leach liquor.

11. The process defined in any one of the 25 preceding claims includes a mixed chloride-sulphate leach which extracts copper from refractory sulphide minerals such as chalcopyrite in the sulphide ore or concentrate or the solid residue of a previous leach step.

30

12. The process defined in claim 11 including carrying out the chloride-sulphate leach with oxygen injection at 80 to 125°C.

13. The process defined in claim 12 includes 35 carrying out the chloride-sulphate leach at atmospheric or low pressure with a chloride level of 5 to 60 g/l.

- 24 -

14. The process defined in claim 12 includes carrying out the chloride-sulphate leach at high pressure with a chloride level of 5 to 15 g/l.

5 15. The process defined in any one of claims 11 to 14 includes carrying out a solids/liquid separation and forming a solid residue and an exit leach liquor.

10 16. The process defined in claim 15 includes recovering copper from the exit leach liquor.

15 17. The process defined in any one of the preceding claims includes an oxidative acid sulphate high pressure leach carried out at over 200°C which converts to sulphate much of the sulphur present in the sulphide ore or concentrate or the solid residue of a previous leach step and extracts copper and zinc.

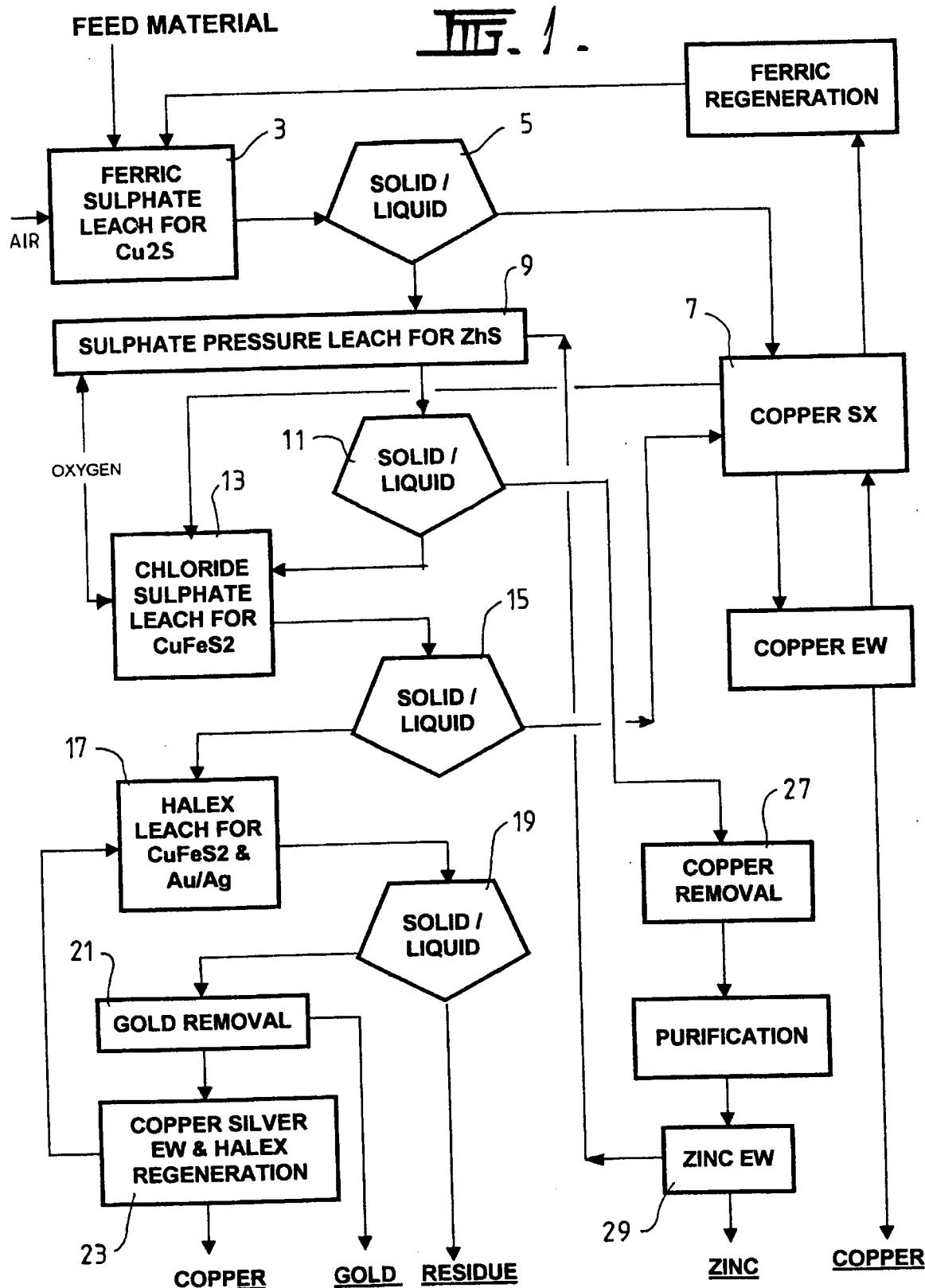
20 18. The process defined in claim 17 includes carrying out a solids/liquid separation and forming a solid residue and an exit leach liquor.

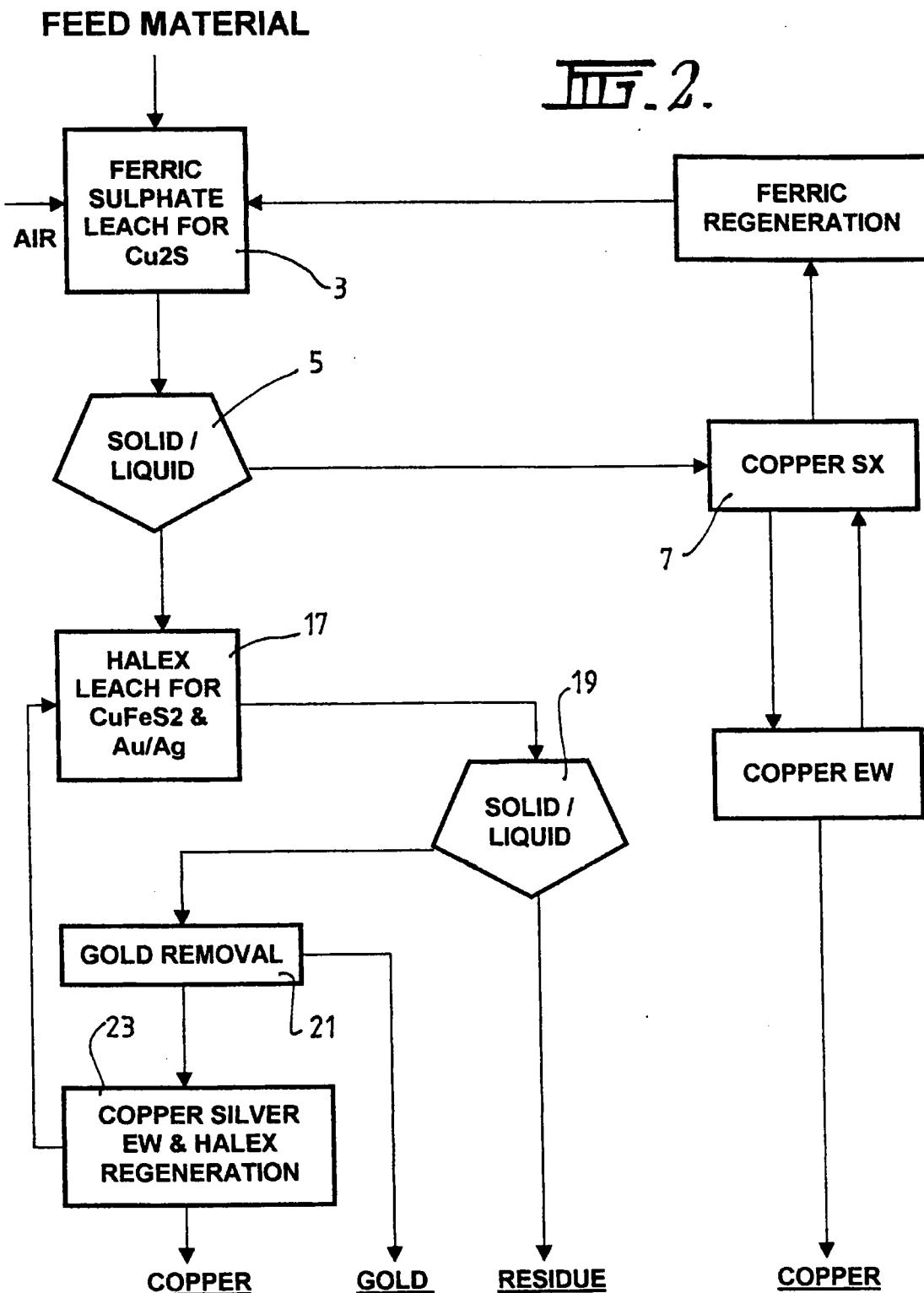
25 19. The process defined in claim 18 includes recovering copper and zinc from the exit leach liquor.

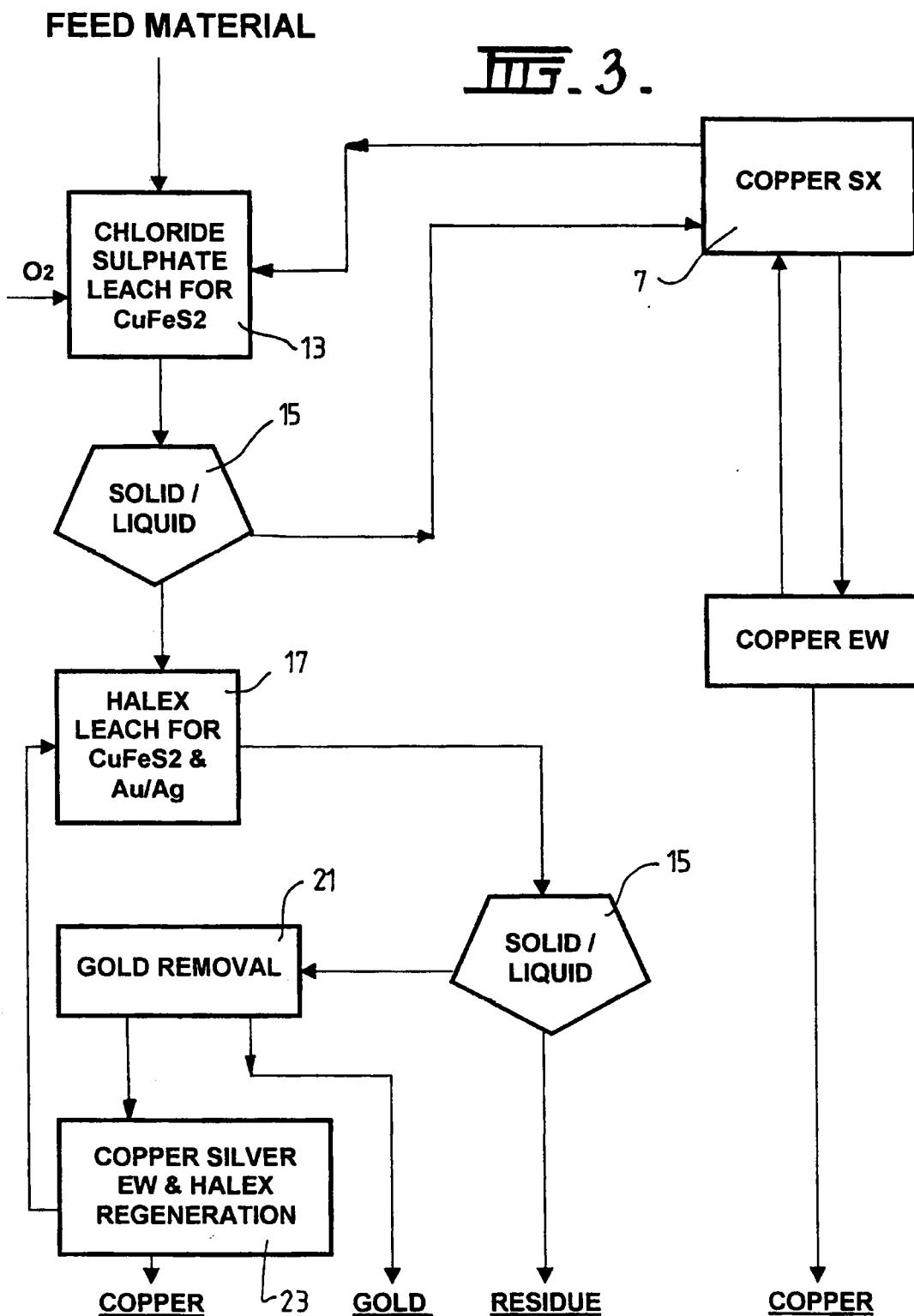
20 20. The process defined in any one of the preceding claims includes a halex leach which extracts copper, silver and gold from the sulphide ore or concentrate or the solid residue of a previous leach step.

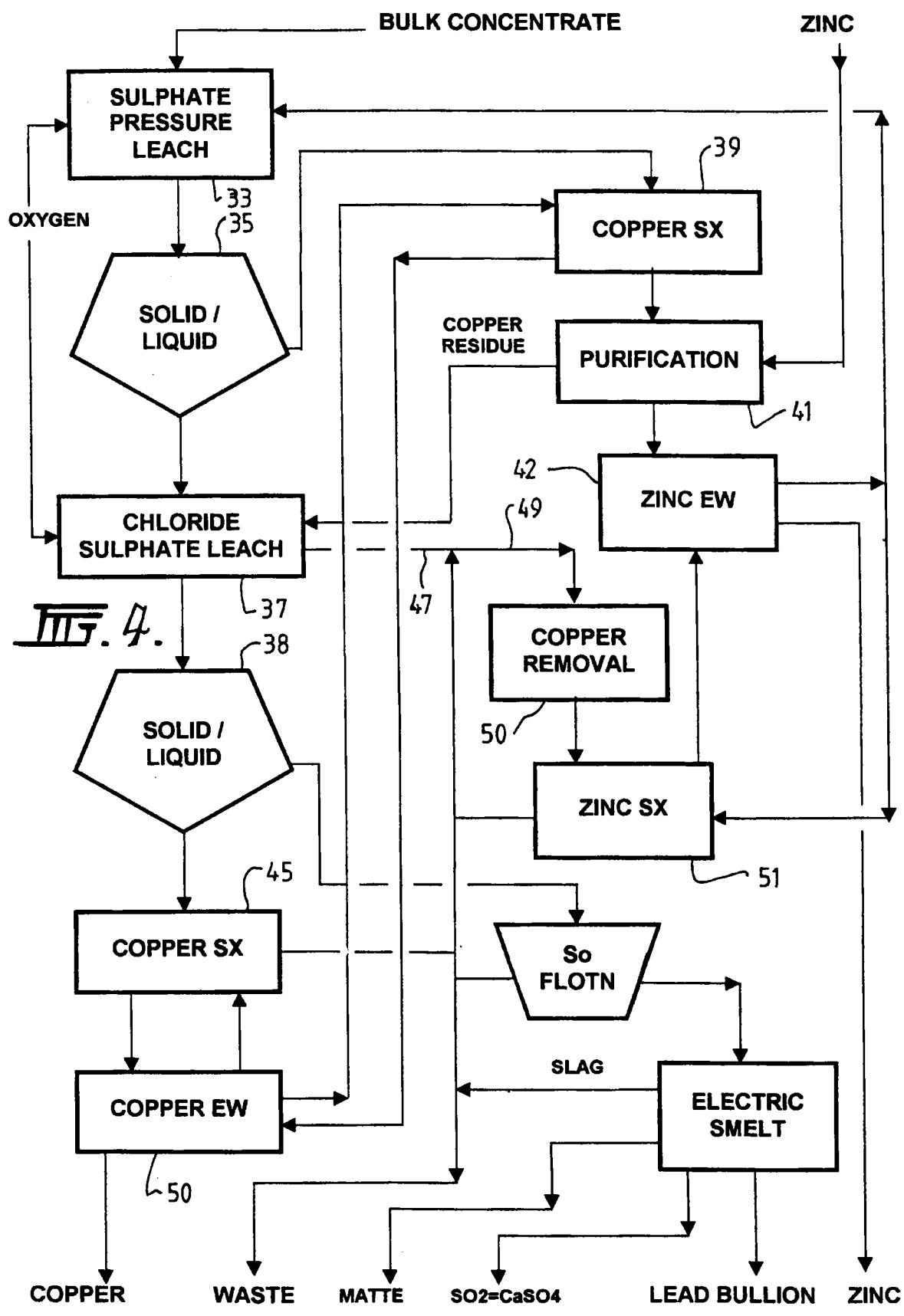
30 21. The process defined in claim 20 includes carrying out a solids/liquid separation and forming a solid residue and an exit leach liquor.

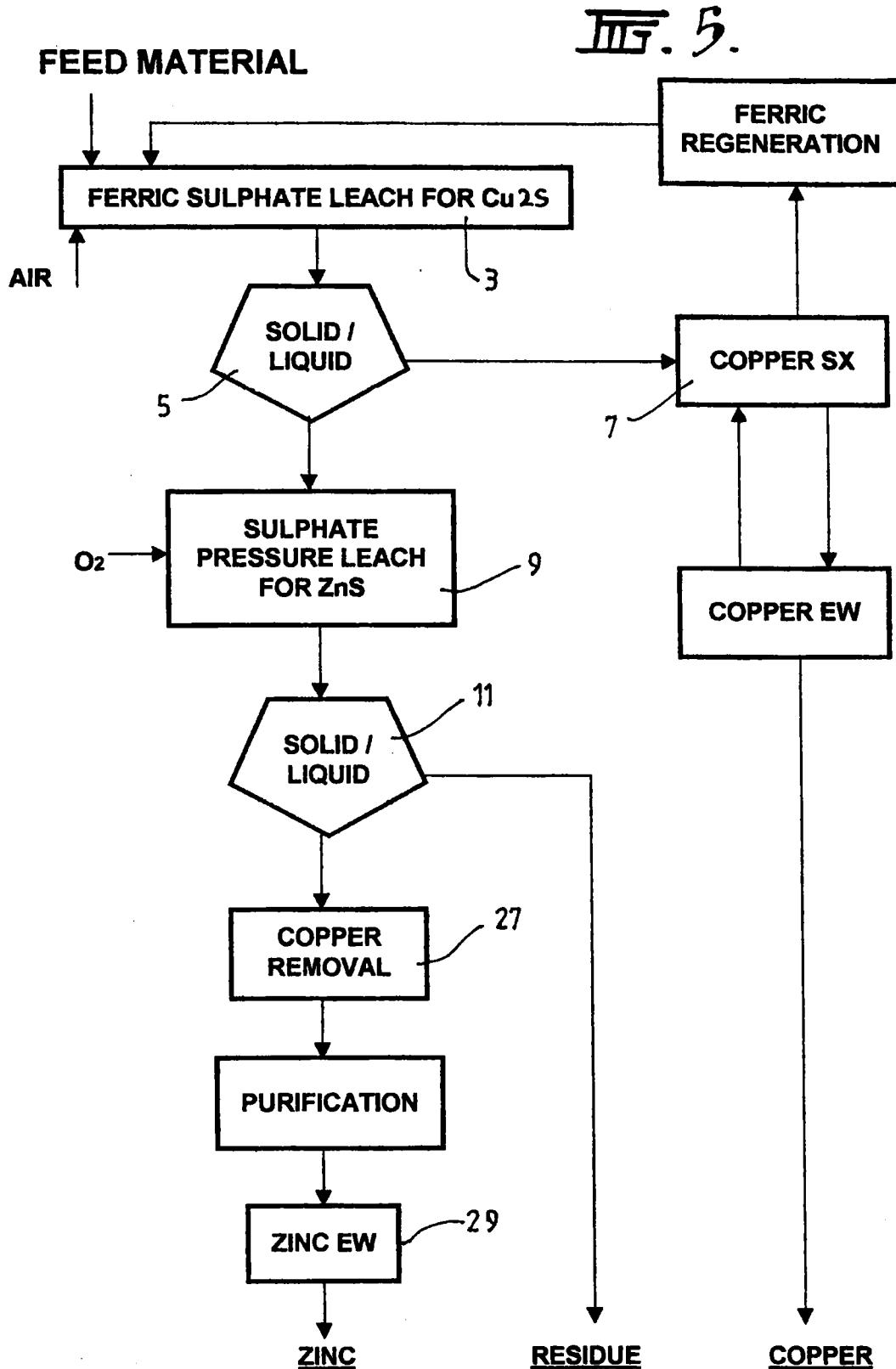
35 22. The process defined in claim 21 includes recovering copper, silver and gold from the exit leach liquor.











INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00679

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C22B 3/06, 3/08, 3/10, 3/22, 3/26, 3/42, 15/00, 19/02, 19/20, 11/00, 11/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C22B 3/06, 3/08, 3/10, 3/22, 3/26, 3/42, 15/00, 19/02, 19/20, 11/00, 11/06		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) ORBIT: Derwent Online Abstracts, keywords (Copper or Cu) & (Zinc or Zn or Silver or Ag or Gold or Au) & (sulphide or sulfide or chalcocite or CuS ₂ or sphalerite or ZnS or chalcopyrite or CuFeS ₂) & leach; period 1975-99.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 4138248 A (NARAIN) 6 February 1979. See abstract.	1, 2 1-6
X Y	US 4337128 (HAAKONSEN et al) 29 June 1982. See abstract.	1, 2 1-6
X Y	Derwent Abstracts Accession No. 98-018951/02, Class D16, ZA 9701307 A (MINTEK) 29 October 1979.	1-6 7-22
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C		<input checked="" type="checkbox"/> See patent family annex
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 15 September 1999	Date of mailing of the international search report - 8 OCT 1999	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929	Authorized officer GRAEME J. BROXAM Telephone No.: (02) 6283 2133 	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00679

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X Y	WO 98/39491 A (PINCHES) 11 September 1998. See claims, examples.	1-6 7-22
X Y	US 4115221 A (WADSWORTH et al) 19 September 1978. See examples.	1-6 7-22
X Y	US 4032330 A (FOUNTAIN et al) 28 June 1977. See examples.	1-6 7-22
X Y	WO 96/19593 A (COMINCO ENGINEERING SERVICES LTD.) 27 June 1996. See whole specification.	1, 2, 7-19 3-6, 20-22
X Y	WO 96/41027 A (COMINCO ENGINEERING SERVICES LTD.) 19 December 1996. See whole specification.	1, 2, 7-19 3-6, 20-22
X Y	WO 96/41026 A (COMINCO ENGINEERING SERVICES LTD.) 19 December 1996. See whole specification.	1, 2, 7-19 3-6, 20-22
X Y	US 4676828 A (ANDRE) 30 June 1997. See whole specification.	1, 2, 7-10 3-6, 11-22
X Y	WO 94/00606 A (EVERETT) 6 January 1994. See whole specification.	20-22 1-19

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 99/00679

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US 4138248	AR	218716	AU	45940/79	BE	875468	
	CA	1114174	DK	5249/79	EP	15938	
	ES	479435	FI	790750	FR	2422588	
	GB	2035982	MX	151470	PH	15344	
	SE	7910115	ZA	7901704	ZM	34/79	
	WO	7900906	US	4236918			
US 4337128	AU	76087/81	CA	1176472	ES	506053	
	ES	8301282	NO	802986	PT	73779	
WO 9839491	AU	22246/97					
US 4115221	NO	FAMILY					
US 4032330	NO	FAMILY					
WO 9619593	CN	1187220	EP	804624	US	5645708	
	US	5431788	US	5855858	US	5869012	
	US	5874055	US	5902474	WO	9619593	
	CA	2208026	AU	12701/95	BG	101726	
	CZ	9701849	FI	972663	HR	950601	
	NO	972836	PL	320939	ZA	9410363	
	ZA	9510710	CA	2099333	AU	42960/96	
	AU	44766/96	AU	58889/96	BG	102132	
	BG	102133	BG	102149	CA	2221781	
	CA	2221930	CA	2221940	CN	1186523	
	CA	1186524	EP	832302	EP	832303	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 99/00679

Patent Document Cited in Search Report				Patent Family Member			
WO	9619593	EP	832306	EP	924307	EP	930373
	(CONT)	FI	974427	FI	974428	NO	975707
		PL	323593	PL	323782	PL	323799
		WO	9641026	WO	9641027	WO	9641029
WO	9641026	SAME AS WO 9619593					
WO	9641027	(ABOVE)					
US	4676828	AU	42713/85	BG	44209	CA	1258180
		DD	232933	EP	166710	ES	543511
		ES	8607418	FI	852098	JP	60255938
		LU	85385	NO	852086	YU	892/85
		ZA	8504052				
WO	9400606	AP	538	AU	42999/93	BR	9306622
		CN	1091157	EP	646185	FI	946086
		HU	72104	MX	9303884	NO	945025
		NZ	252952	US	5487819	ZA	9304594

END OF ANNEX